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(54) PREPARATION OF DISPERSION OF COLORED RESIN PARTICLE IN WATER

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a water-base ink for ink jet recording which does not sacrifice features inherent in a resin dispersion type water-base ink, i.e., excellent print quality, water resistance, lightfastness, has excellent dispersion stability, and can be stably ejected by ink jetting without causing nozzle clogging by a process for preparing a dispersion of a colored resin particle, having a small diameter and possessing excellent dispersion stability, in water.

SOLUTION: This process for preparing a dispersion of a colored resin particle in water comprises the steps of: (1) dispersing or dissolving at least a colorant in a resin having an acid value to prepare a solid, colored compound; (2) mixing at least water, an org. solvent capable of dissolving a resin, a base, and the solid, colored compd. prepd. in the step of coloring of the resin together followed by stirring and/or dispersion to prepare a colorant suspension with at least a part of the resin being dissolved therein; and (3) depositing a dissolved resin component in the colorant suspension prepd. in the step of suspension onto the surface of the colorant in the colorant suspension.

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CLAIMS

[Claim(s)]

[Claim 1] The coloring resin particle water dispersion manufacture approach of obtaining a coloring resin particle water dispersion at the following process.

- (1) The resin coloring process of distributing or dissolving a coloring agent in the film-forming resin which has the acid number at least, and obtaining a solid coloring compound.
- (2) The suspension process which obtains the coloring agent suspension which mixes at least water, the organic solvent which dissolves film-forming resin, a base, and the solid coloring compound obtained at said resin coloring process, and some resin is dissolving at least by distribution.
- (3) The reprecipitation process to which the coloring agent front face in the coloring agent suspension obtained at said suspension process is made to carry out the deposition of the dissolution resinous principle.

[Claim 2] The coloring resin particle water dispersion manufacture approach according to claim 1 which uses together the hydrophilic organic solvent which does not dissolve film-forming resin in the organic solvent which dissolves film-forming resin substantially further.

[Claim 3] the reprecipitation process of (3) -- the coloring resin particle water dispersion manufacture approach according to claim 1 which deliquors from suspension the organic solvent which is, and adds the water or the aqueous medium which functions on the coloring agent suspension of the suspension process of (2) which resin is dissolving as a poor solvent to resin, or dissolves resin.

[Claim 4] the reprecipitation process of (3) -- the coloring resin particle water dispersion manufacture approach according to claim 1 which deliquors from suspension the organic solvent which dissolves resin after adding the water or the aqueous medium which functions on the coloring agent suspension of the suspension process of (2) which is and resin is dissolving as a poor solvent to resin.

[Claim 5] The coloring resin particle water dispersion manufacture approach according to claim 1 which distributes it in the resin coloring process of (1) to the resin which has the acid number under high shearing force, using a pigment as a coloring agent.

[Claim 6] Using the solid coloring compound obtained as a compound, using carbon black as a coloring agent, subsequently to the suspension process of (2) perform the reprecipitation process of (3) promptly, or as a compound The coloring resin particle water dispersion manufacture approach according to claim 1 of establishing the process which diameter [of a granule]-izes the color particle in coloring agent suspension more under high shearing force between the suspension process of (2), and the reprecipitation process of (3) while using the solid coloring compound obtained using an organic pigment as a coloring agent.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the coloring resin particle water dispersion manufacture approach.

[0002]

[Description of the Prior Art] Although the ink for ink jet record has oily ink and water color ink when it is divided roughly, oily ink has a problem an odor and in respect of toxicity, and is becoming in use [water color ink].

[0003] However, since many of conventional water color ink used water soluble dye as a coloring agent, it had the fault that a water resisting property and lightfastness were bad. Moreover, since the color was dissolving with the molecular level, when printed in the so-called regular papers, such as a copy paper currently generally used in office, the bleeding called a mustache-like feather ring was produced and remarkable deterioration of printing quality had been caused.

[0004] The various proposals of the pitch powder type ink which connotes a coloring agent as ink, or the polymeric latex or the microcapsule of the resin dissolution mold which the so-called water pigment ink was variously proposed [mold] in the past in order to improve the above-mentioned fault, for example, distributed carbon black and an organic pigment, using water soluble resin as a binder-cum-a dispersant are made.

[0005] As watercolor pigment ink for jet printers The color particle distributed if possible by the diameter of a particle is called for. As an example of the water color ink of a concrete resin dissolution mold in the patent No. 2512861 official report (a) -- a pigment and a polymer dispersant -- 2-roll milling equipment -- being filled up -- ; (b) grinding -- carrying out -- the dispersing element of a pigment and a polymer dispersant -- obtaining --; and (c) -- it consists of a process which distributes this pigment dispersing element in an aqueous carrier medium -- The adjustment approach of the water ink for the ink jets containing a pigment of having the improved property in JP,3-153775,A a) -- ink jet printing containing the organic solvent c wetting-agent d water which can be diluted with the solid-state pigment formulation b water containing a pigment and carboxyl group content Pori acrylic resin -- service water -- the sex ink constituent is proposed.

[0006] However, these techniques are the effects of the dispersant resin which is dissolving the thing effective in atomization of a pigment, tended to produce the abnormality injection by ink viscosity lifting near a nozzle, and the worst nozzle blinding with moisture evaporation of ink, and were remarkably inferior in the water resisting property of a print.

[0007] There is an advantage of viscosity lifting accompanying moisture evaporation of ink having comparatively little pitch powder type water color ink, and excelling in a water resisting property. The ink constituent which specifically contains the urethane polymer latex which contained the color in JP,58-45272,A, In JP,62-95366,A, a polymer and fat dye are dissolved into a water-insoluble nature organic solvent. The ink containing the color which evaporated the solvent and was connoted in the polymer particle after mixing with the water solution which furthermore contains a surface active agent and making it emulsify is proposed. The manufacturing method of the coloring agent aqueous suspension by making boundary tension between the organic solvent at the time of capsulation and water into 10 dynes or less in JP,62-254833,A is proposed. Although the recording ink containing the coloring matter which carried out macro capsulation similarly etc. is proposed in JP,1-170672,A It was not necessarily enough, and the distributed stability of the coloring resin distribution object obtained by them had large foaming under the effect of the surface active agent used at the time of capsulation, and was not necessarily enough. [of the injection property of an ink jet]

[0008]

[Problem(s) to be Solved by the Invention] The technical problem which this invention tends to solve is to offer the coloring resin particle water dispersion manufacture approach of having excelled in distributed stability with the diameter of a particle.

[0009]

[Means for Solving the Problem] this invention person etc. came to solve this invention, as a result of repeating

research wholeheartedly, in order to solve the above-mentioned technical problem. That is, this invention offers the next invention.

[0010] The coloring resin particle water dispersion manufacture approach of obtaining a coloring resin particle water dispersion at the following process.

(1). The resin coloring process of distributing or dissolving a coloring agent in the film-forming resin which has the acid number at least, and obtaining a solid coloring compound.

(2) The suspension process which obtains the coloring agent suspension which mixes at least water, the organic solvent which dissolves film-forming resin, a base, and the solid coloring compound obtained at said resin coloring process, and some resin is dissolving at least by distribution.

(3) The reprecipitation process to which the coloring agent front face in the coloring agent suspension obtained at said suspension process is made to carry out the deposition of the dissolution resinous principle.

[0011] The resin coloring process of (1) of this invention is a process which distributes or dissolves a coloring agent in the film-forming resin which has the acid number at least, and obtains a solid coloring compound. Using kneading equipments known conventionally, such as a roll, a kneader, and a bead mill, this process is in a solution or the condition by which heating melting was carried out, can make the film-forming resin which has the acid number able to dissolve or distribute a coloring agent to homogeneity, and can be performed by taking out as a solid-state kneading object (solid coloring compound) eventually.

[0012] In this invention, in using the coloring resin particle water dispersion obtained eventually as jet ink, it is made to realize injection which does not have blinding as jet ink and was stabilized. For example, the micro-disperse to the film-forming resin which has the acid number of a pigment in using a pigment as a coloring agent is required, and it is desirable to adopt a distributed means by which the condition that high shearing force is relatively applied among the distributed approaches learned conventionally is formed, and to distribute under high shearing force as a means to distribute a pigment. As such a suitable means, it is desirable to use 2 rolls.

[0013] What is necessary is on the other hand, just to dissolve a color in resin simply by carrying out micro-disperse of the color into resin using kneading equipment like a pigment, if the dissolution to resin is possible for a color when a coloring agent is a color.

[0014] The suspension process of (2) of this invention is a process which obtains the coloring agent suspension which mixes at least water, the organic solvent which dissolves film-forming resin, a base, and the solid coloring compound obtained at said resin coloring process, and some resin is dissolving at least by distribution.

[0015] To the organic solvent which dissolves the film-forming resin which has water and the acid number for the solid coloring compound obtained at the resin coloring process of (1) as a dispersion medium, and the mixed solvent which makes a base indispensable, in addition, by agitating so that it may distribute to homogeneity The coat nature resin which has the acid number which includes a coloring agent borrows the assistance of an organic solvent and a base, and dissolves or emulsifies [self-], and the coloring agent suspension in which some of resin concerned is dissolving at least in any case is obtained from a solid coloring compound front face.

[0016] As for the film-forming resin which has the acid number which exists in the front face of a solid coloring compound according to this process, at least a part or all of that acid number is gradually neutralized by the base, and mixture will be in a suspension condition from the solid-state configuration of the compound concerned.

[0017] When the resin concerned is dissolving in said solvent object thoroughly, the ***** front face has exposed the coloring agent in suspension, but when resin is carrying out self-emulsification, it is thought at least that a part of coloring agent front face is covered with resin. What a coloring agent may dissolve in the resin concerned is considered in suspension that it is in a colloidal state.

[0018] As the stirring approach for obtaining suspension, each technique of well-known common use can adopt, for example, it can suspend easily besides the stirring aerofoil of the propeller mold of one conventional shaft using the stirring aerofoil and stirring container of a configuration according to the object.

[0019] Or there is no shearing force, when in obtaining suspension it is only small mere mixed stirring relatively or is comparatively easy to condense a coloring agent, in addition to it, further subsequently to the bottom of high shearing force, distribution may be stabilized more. As for re-condensation of a coloring agent, it is desirable to use the bead loess distribution equipment known for a high voltage homogenizer, a trade name Micro fluidizer, or a nano mizer as a disperser in this case few.

[0020] For example, since the coloring agent suspension comparatively distributed in the diameter of a granule is obtained at the suspension process of (2) when using the solid coloring compound obtained as a compound, using carbon black as a coloring agent, subsequently the reprecipitation process of (3) can be performed promptly. In using the solid coloring compound using an inorganic pigment including the case where the solid coloring compound obtained as a compound, using an organic pigment as a coloring agent is used on the other hand, or carbon black In order to diameter[of a granule]-ize more the color particle in the coloring agent suspension which obtains the suspension obtained from a former compound between the suspension process of (2), and the reprecipitation process of (3) from a latter compound since distributed stability is increased more It

is desirable to prepare the process which exposes the suspension concerned and is distributed in the bottom of high shearing force.

[0021] The reprecipitation process of (3) of this invention is a process to which the coloring agent front face in the coloring agent suspension obtained at said suspension process is made to carry out the deposition of the dissolution resinous principle concerned. In this invention, "reprecipitation" does not mean carrying out separation sedimentation of a coloring agent or the coloring agent with which the dissolution resin concerned stuck to the coloring agent front face from the solvent object of suspension. Therefore, what is obtained at this process is coloring resin particle aqueous dispersion liquid which not the mere mixture in which the formed element and the liquid component carried out clear separation but the coloring agent with which the dissolution resin concerned stuck to the coloring agent front face distributed stably on the solvent object of suspension.

[0022] the coloring agent front face in the coloring agent suspension of this suspension process of (2) -- the deposition of dissolution resin -- for example, ** -- it can carry out easily by carrying out by adding the water or the aqueous medium which functions on the coloring agent suspension which the resin concerned is dissolving in part at least as a poor solvent to the resin concerned, or carrying out by removing an organic solvent from ** coloring agent suspension.

[0023] However, there are also few aggregates and the approach of performing by adding the water or the aqueous medium which functions on coloring agent suspension as a poor solvent to the resin concerned is desirable. By dropping water or an aqueous medium, stirring suspension loosely, it becomes possible to make a coloring agent front face carry out the deposition (reprecipitation) of the resin certainly of reprecipitation, preventing generating of an aggregate.

[0024] Thus, in (3), although the coloring resin particle of desired particle diameter is obtained, that mean-particle-diameter range is usually 0.01–20 micrometers. In addition, when using dispersion liquid as recording ink for ink jets eventually, it is desirable to make mean particle diameter set to 3–15 micrometers, submicron order (less than 1 micrometer), then in are good, removing a solvent object from dispersion liquid and using as a dry type toner for the static electricity **** development.

[0025] Thus, although the obtained coloring resin particle water dispersion can also be used as it is, deliquoring further is desirable, since a coloring resin particle is in a swelling condition under the effect of the organic solvent which lives together in order to raise preservation stability more, or in order to raise the safety to a fire or a public nuisance more. Moreover, what is necessary is just to perform deliquoring and dehydration using distillation, a centrifugal separation and ** exception, etc., in using a coloring resin particle as fine particles.

[0026] Thus, without destroying by fire, in aiming at a mass production, in a closed system, it can recycle and the removed organic solvent can also be reused.

[0027] The film-forming resin used for the coloring resin particle water dispersion manufacture approach of this invention has the acid number. The acid numbers of desirable resin are 10–280, and the neutralization index by the base of the suspension process of (2) is more than 10 mol % of the acid radical of resin as an example that what is necessary is just to be more than extent in which the resin concerned of (1) carries out self-emulsification into suspension. Since in the case of high acid-number resin the solubility of the resin to the inside of suspension will increase if the neutralization index by the base becomes high, as for the amount of the base used, it is desirable to adjust suitably based on the size of the path which the particulate material of dissolution extent to a solvent object or the water dispersion obtained eventually means.

[0028] That what is necessary is just resin which forms a coat, the film-forming resin concerned is limited to neither natural resin nor synthetic resin, various resin can use it, for example, styrene resin, acrylic resin, polyester system resin, and polyurethane system resin are mentioned. The resin concerned may have the bridge formation of the reversible property which will be in the condition of not constructing a bridge, with heat although the bridge is constructed in ordinary temperature even if permanent bridge formation is carried out without a heat dependency.

[0029] In this invention, resin desirable as film-forming resin is the copolymer of at least one monomer chosen from the group which consists of styrene, permutation styrene, and acrylic ester (meta), and acrylic acid (meta).

[0030] Film-forming resin covers in a compound the coloring agent which is carrying out micro-disperse, and makes possible the ultrafine particle coloring resin particle water dispersion which was extremely excellent in distributed stability at the same time it carries out self-emulsification in a suspension process (2). Although especially a limit does not have the molecular-weight range of resin, in the case of styrene resin or acrylic resin, the thing of or more 1000 100,000 or less molecular weight is more desirable.

[0031] the coloring resin particle water dispersion of the submicron order obtained by the coloring resin particle water dispersion manufacture approach of this invention -- ink jet record -- service water -- when it uses as sex ink, the ink jet fitness excellent in distributed stability and an injection property is shown. When applying the coloring resin particle water dispersion manufacture approach of this invention to this, and the suspension in the suspension process of (2) makes a desiccation inhibitor contain, water color ink is obtained by the suspension and the water dispersion pan which were extremely excellent in distributed stability.

[0032] Moreover, as a base in the suspension process of (2), alcoholic amines, such as triethanolamine besides alkalis, such as a hydroxide of alkali metal, such as a sodium hydroxide, a potassium hydroxide, and a lithium hydroxide, ammonia, triethylamine, and a morpholine, diethanolamine, and N-methyldiethanolamine, are usable, for example.

[0033] Since the deposition of the resin on the front face of a coloring agent becomes inadequate in the reprecipitation process of (3), as for the addition of the base in the inside of suspension, it is desirable [if high acid-number resin is neutralized using a strong base, the organic solvent which the solubility of the resin to water increases and dissolves resin will become unnecessary, but] the strength of a base and to carry out the amount-used (neutralization index) accommodation so that a water-soluble-resin component may not increase.

[0034] Especially in the case of the water color ink for ink jet record, since an adverse effect is in the blinding of a nozzle, the distributed stability at the time of preservation, and the water resisting property of a print, it is desirable to press down this water-soluble-resin component to the minimum. An alcoholic amine, especially triethanolamine have little generating which is said water-soluble-resin component in a weak base, and it is the optimal base for preparation of the water color ink for ink jet record.

[0035] Although not things limited but each coloring agent of well-known common use can use it especially for the coloring resin particle water dispersion manufacture approach of this invention, colors, such as aquosity colors and fat dye, such as monoazo besides organic pigments, such as azo pigments, such as inorganic pigments, such as carbon black, black titanium oxide, a titanium white, zinc sulfide, and red ocher, and a phthalocyanine pigment, monoazo, a JISUAZO system, a phthalocyanine pigment, and a quinacridone pigment, a JISUAZO system, a metallic complex system, an anthraquinone system, and a triaryl methane system, and a disperse dye, are used, for example. The coloring resin coat which excelled [be / the way which uses a pigment / a twist using a color] in the water resisting property is easy to be obtained.

[0036] In obtaining an achromatic color coloring resin particle division black coloring resin particle, in order for what is necessary to be just to use the coloring agent which made carbon black or it the subject and to obtain a chromatic color coloring resin particle, it is desirable to use an organic pigment. It is the suspension process of (2) and it is easy for the bottom of the same manufacture condition for carbon black to consider as the diameter of a granule from an organic pigment as described above.

[0037] Although the amount of this coloring agent used is prepared so that it may become the amount which usually becomes 0.5 – 20 % of the weight in the coloring resin particle dispersion liquid obtained eventually, although it will not be specified especially if the effectiveness in this invention is attained, it is desirable. It is also the same as when obtaining the water color ink for jet record.

[0038] the coloring resin particle water dispersion which the dispersion medium used for the suspension process of (2) is water on which a subject functions as a poor solvent, and is obtained eventually — ink jet record — service water — the case where it uses as sex ink — each process **** of this invention — as for a solvent object, in all the processes performed additionally, it is desirable to have the purity more than ion exchange water.

[0039] Although the organic solvent which dissolves the film-forming resin which has the acid number is used in this invention, this functions as a good solvent to the resin concerned. It is usable, if it can choose suitably to the resin concerned as the organic solvent concerned, for example, resin, such as glycol ether system solvents, such as ester solvent, such as aromatic series system solvents, such as chlorine-based solvents, such as alcoholic solvent, such as ketone solvent, such as an acetone, dimethyl ketone, and a methyl ethyl ketone, a methanol, ethanol, and isopropyl alcohol, chloroform, and a methylene chloride, benzene, and toluene, and ethyl-acetate ester, ethylene glycol monomethyl ether, and ethylene glycol wood ether, and amides, is dissolved.

[0040] At the suspension process of (2), it is desirable that the mixed liquor of water and an organic solvent is uniform, and when not uniform, it is desirable to make an O/W mold emulsify mechanically, using a surfactant, or to use an assistant solvent together, to make it equalize, and to use.

[0041] That is, although you may make it only it used for them, the organic solvents which dissolve the film-forming resin which forms a dispersion medium, and which has the acid number are only it, water, and a base, and they use together in part the hydrophilic organic solvent which does not dissolve the film-forming resin which has the acid number for the coloring agent suspension excellent in distributed stability in it in being difficult to get as an assistant solvent, and you may make it give better stability. In addition, each of organic solvents which dissolve the film-forming resin which has the acid number, and organic solvents which does not said-dissolve may use together one sort or two sorts or more.

[0042] In the case of the copolymer of at least one monomer chosen from the group which the film-forming resin concerned becomes from styrene, permutation styrene, and acrylic ester (meta), and acrylic acid (meta), at least one or more kinds of combination chosen from alcoholic solvent, such as isopropyl alcohol, mainly as an assistant solvent in ketone solvent, such as a methyl ethyl ketone, is good.

[0043] Although the ratio of this water and organic solvent will not be specified especially if the effectiveness in this invention is attained, its amount from which the weight ratio of water/organic solvent is set to 10 / 1 – 1/1

is desirable. When using together the hydrophilic organic solvent which does not dissolve film-forming resin, as for the amount used, minimizing is desirable also from the point which should make the dispersion medium the solvent object which does not contain an organic solvent for the dispersion liquid obtained eventually as much as possible, and the point which mitigates more the burden of separation recovery processing of a partially aromatic solvent.

[0044] A dispersant, a plasticizer, an antioxidant, an ultraviolet ray absorbent, etc. may be used for the above-mentioned organic solvent as an additive if needed, and you may add to the coloring process of (1) similarly.

[0045] Moreover, in using the dispersion liquid obtained above as ink for ink jet record, in order to prevent desiccation of ink, it is desirable to make a desiccation inhibitor exist in the ink concerned. What is necessary is just to add the desiccation inhibitor concerned directly to the suspension process of (2), or the coloring resin particle water dispersion obtained eventually.

[0046] This desiccation inhibitor gives the effectiveness of preventing desiccation of the ink in injection nozzle opening of an ink jet, and what has the boiling point more than the boiling point of the indifferent water is used. Although each thing of the well-known common use known conventionally can use it as such a desiccation inhibitor, there are polyhydric alcohol or those alkyl ether, such as ethylene glycol, propylene glycol, a diethylene glycol, dipropylene glycol, a polyethylene glycol, a polypropylene glycol, and a glycerol, etc., for example.

[0047] Although the amount of the desiccation inhibitor used changes with classes, it is usually suitably chosen from the range of the 1 – 150 weight section to the water 100 weight section.

[0048] especially -- the manufacture approach of this invention -- ink jet record -- service water -- when applying to the manufacture approach of sex ink and a glycerol is a desiccation inhibitor, the desiccation prevention effectiveness of having excelled most is shown. When usually using that with which only the glycerol used other desiccation inhibitors together to it to the water 100 weight section, 10 – 50 weight section is suitable for the amount of the glycerol used.

[0049] especially -- the manufacture approach of this invention -- ink jet record -- service water -- when applying to the manufacture approach of sex ink, additives, such as a surfactant for osmosis on the water-soluble organic solvent in which the permeability grant effectiveness is shown, water soluble resin, pH regulator, and distribution, defoaming and paper, antiseptics, and a chelating agent, can be added if needed as a permeability grant agent for making ink permeate well in paper.

[0050] When mixing the self-water-dispersion resin solution and aqueous medium containing a coloring agent, it may add, or these additives may be added after those mixing, even if it adds in an aqueous medium beforehand.

[0051] especially -- the manufacture approach of this invention -- ink jet record -- service water -- the ink jet record which the filter of a desired particle size was made to pass, usually filtered, and only the particle smaller than the diameter of a nozzle of an ink jet recording apparatus distributed on the solvent object although the dispersion liquid obtained when applying to the manufacture approach of sex ink could be used as water color ink as it was -- service water -- an activity is presented as sex ink. Therefore, it is better for adding an additive after the last filtration preferably to avoid in the case of this application.

[0052] The coloring resin particle obtained by the coloring resin particle water dispersion manufacture approach of this invention The application to other general ink besides sex ink, a coating, and a light filter is possible. ink jet record since it excels in transparency, color enhancement, and distributed stability in the condition of the fine particles which are in the condition of dispersion liquid or were dried -- service water -- Moreover, since particle diameter is also controllable to arbitration, it is applicable also to the field of the toner for electrostatic-charge development etc. with the acid number of resin, and the combination of the neutralization index by the base.

[0053]

[Embodiment of the Invention] This invention includes the following operation gestalt.

[0054] 1. Coloring resin particle water dispersion manufacture approach of obtaining coloring resin particle water dispersion at following process.

(1) The resin coloring process of distributing or dissolving a coloring agent in the film-forming resin which has the acid number at least, and obtaining a solid coloring compound.

(2) The suspension process which obtains the coloring agent suspension which mixes at least water, the organic solvent which dissolves film-forming resin, a base, and the solid coloring compound obtained at said resin coloring process, and some resin is dissolving at least by distribution.

(3) The reprecipitation process to which the coloring agent front face in the coloring agent suspension obtained at said suspension process is made to carry out the deposition of the dissolution resinous principle.

[0055] 2. Coloring resin particle water dispersion manufacture approach of one above-mentioned publication which uses together hydrophilic organic solvent which does not dissolve film-forming resin in organic solvent which dissolves film-forming resin substantially further.

[0056] the reprecipitation process of 3. (3) -- the coloring resin particle water dispersion manufacture approach of the above 1 or two publications which deliquor from suspension the organic solvent which is, and adds the

water or the aqueous medium which functions on the coloring agent suspension of the suspension process of (2) which resin is dissolving as a poor solvent to resin, or dissolves resin.

[0057] the reprecipitation process of 4. (3) -- the coloring resin particle water dispersion manufacture approach of the above 1 or two publications which are, and deliquescent from suspension the organic solvent which dissolves resin after adding the water or the aqueous medium which functions on the coloring agent suspension of the suspension process of (2) which resin is dissolving as a poor solvent to resin.

[0058] The coloring resin particle water dispersion manufacture approach of the above 1 - 4 publication which distributes it in the resin coloring process of 5. (1) to the resin which has the acid number under high shearing force, using a pigment as a coloring agent.

[0059] The coloring resin particle water dispersion manufacture approach of the above 1 - 4 publication which distributes it in the resin coloring process of 6. (1) to the resin which has the acid number using 2 rolls, using a pigment as a coloring agent.

[0060] Using Solid Coloring Compound Obtained as a Compound, Using Carbon Black as a Coloring Agent, Subsequently to Suspension Process of (2) Perform Reprecipitation Process of (3) Promptly, or 7. As a Compound The coloring resin particle water dispersion manufacture approach of the above 1 - 6 publication of establishing the process which diameter [of a granule]-izes the color particle in coloring agent suspension more under high shearing force between the suspension process of (2), and the reprecipitation process of (3) while using the solid coloring compound obtained using an organic pigment as a coloring agent.

[0061] 8. Coloring resin particle water dispersion manufacture approach of one to 7 above-mentioned publication that film-forming resin which has the acid number is film-forming resin which has acid radical of the acid numbers 10-280, and base is more than 10 mol % of acid radical of film-forming resin that has acid radical.

[0062] 9. Coloring resin particle water dispersion manufacture approach of one to 7 above-mentioned publication which is copolymer of at least one monomer chosen from group which film-forming resin which has the acid number becomes from styrene, permutation styrene, and acrylic ester (meta), and acrylic acid (meta).

[0063] It is as follows, when the case where the gestalt of suitable operation of this invention is applied to the ink for ink jet record is made into an example and it explains.

[0064] (1) To the film-forming styrene-(meta) acrylic-acid copolymer resin which has the acid number based on a carboxyl group, use 2 rolls, distribute the pigment as a coloring agent, and obtain a solid coloring compound.

[0065] (2) Use together ***** which does not mainly dissolve said resin for the right organic solvent which dissolves water and said resin substantially so that the rate of a former good solvent may become large, prepare the solution which contains the alcoholic amine as a base, and a desiccation inhibitor respectively and which uses water as the main solvent object, mix the chip of the solid coloring compound of said process (1) to it, and obtain coloring agent suspension by stirring to it. More suitably, it atomizes further so that high shearing force can be given and there may be no re-condensation about suspension using the nano mizer (trademark) which is the disperser from which more sufficient suspension condition is acquired.

[0066] (3) Stirring coloring agent suspension, the water solution containing a desiccation inhibitor is dropped and obtain a coloring resin particle water dispersion.

[0067] From the obtained coloring resin particle water dispersion, an organic solvent is distilled off and it considers as the ink base. the filtration after adding the drugs for ink adjustment to this ink base and adjusting concentration and physical properties to it -- carrying out -- ink jet record -- service water -- it considers as sex ink.

[0068]

[Example] Next, an example and the example of a comparison are given and this invention is explained still more concretely. In addition, the "section" in the following examples expresses the "weight section."

[0069] (Example 1) The 2 roll kneading object of the carbon black 20 section and the styrene-acrylic-acid-methacrylic resin (styrene / acrylic-acid / methacrylic-acid =77/10/13; molecular weight 50,000 and acid number 160) 20 section was put into the mixed solution of the water 210 section, the glycerol 35 section, the triethanolamine 8 section, the methyl-ethyl-ketone 90 section, and the isopropyl alcohol 40 section, it stirred at the room temperature for 3 hours, and coloring agent suspension was obtained.

[0070] Stirring to the obtained suspension, the mixed liquor of the glycerol 30 section and the water 210 section was dropped at the rate of 5ml/m, and the black coloring resin particle water dispersion was obtained. A methyl ethyl ketone and isopropyl alcohol were distilled off for the obtained capsule liquid using the rotary evaporator, and the last black coloring resin particle water dispersion was obtained.

[0071] use 1-micrometer filter for this water distribution object -- a fault -- carrying out -- ink jet record -- service water -- it considered as sex ink.

[0072] There is also no aggregate, stable distribution was shown over the long period of time, printing using a piezo type ink jet printer was stable, the microcapsule in the obtained water color ink has the mean particle diameter of 0.09 micrometers, and, moreover, it was [the obtained print does not have a blot, either, showed whenever / high / black /, and] excellent in waterproof lightfastness.

[0073] (Example 1 of a comparison) Although it is the suspension presentation of an example 1 except having removed the methyl ethyl ketone (right organic solvent which dissolves film-forming resin) and the 2 roll kneading object was stirred like the example 1, the kneading object was not able to be dissolved, and suspension was not able to obtain and ink-ize it.

[0074] (Example 2) The 2 roll kneading object of the quinacridone pigment 40 section and the styrene-acrylic-acid-methacrylic resin (styrene / acrylic-acid / methacrylic-acid =77/10/13; molecular weight 50,000 and acid number 160) 40 section In the place which put into the mixed solution of the water 250 section, the glycerol 22 section, the triethanolamine 8 section, the methyl-ethyl-ketone 90 section, and the isopropyl alcohol 40 section, and stirred at the room temperature for 3 hours, and the kneading object dissolved It distributed by the pressure of 98MPa(s) using the collision type disperser nano mizer (nano mizer company make), and coloring agent suspension was obtained.

[0075] Stirring to the obtained suspension, the mixed liquor of the glycerol 22 section and the water 250 section was dropped at the rate of 5ml/m, and Magenta color coloring resin particle dispersion liquid were obtained. A methyl ethyl ketone and isopropyl alcohol were distilled off for the obtained capsule liquid using the rotary evaporator, and the last Magenta color coloring resin particle water dispersion was obtained.

[0076] use 1-micrometer filter for this water distribution object -- a fault -- carrying out -- ink jet record -- service water -- it considered as sex ink.

[0077] The coloring resin particle in the obtained water color ink had the mean particle diameter of 0.12 micrometers, and there is also no aggregate, stable distribution was shown over the long period of time, printing using a piezo type ink jet printer was stable, the obtained print does not have a blot, either, the very vivid high Magenta color of a feeling of transparence was shown, and, moreover, it excelled in waterproof lightfastness.

[0078]

[Effect of the Invention] the coloring resin particle in the coloring resin particle water dispersion obtained by the coloring resin particle water dispersion manufacture approach of this invention -- the diameter of a particle -- it is -- very -- distributed stability -- excelling -- **** -- for example , ink-jet record -- service water -- the ink-jet injection property which is excellent in distributed stability , and does not have nozzle blinding , either , and was stabilized makes possible , without killing the features of pitch powder type water color ink excellent in printing quality , a water resisting property , and lightfastness , if it applies to sex ink .

[Translation done.]

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(54)【発明の名称】 着色樹脂粒子水分散液製造方法

(57)【要約】

【課題】 微粒子径で分散安定性に優れた着色樹脂粒子水分散液製造方法により、印刷品質・耐水性・耐光性に優れた樹脂分散型水性インクの特長を殺すことなく、分散安定性に優れ、かつノズル目詰まりもなく、安定したインクジェット噴射特性可能なインクジェット記録用水性インクを得る。

【解決手段】 下記工程にて着色樹脂粒子水分散液を得る着色樹脂粒子水分散液製造方法。

(1) 酸価を有する樹脂に少なくとも着色剤を分散または溶解して固形着色コンパウンドを得る樹脂着色工程。

(2) 少なくとも、水、樹脂を溶解する有機溶剤、塩基、樹脂着色工程で得られた固形着色コンパウンドを混合し、攪拌及び／または分散によって少なくとも樹脂の一部が溶解している着色剤懸濁液を得る懸濁工程。

(3) 懸濁工程で得られた着色剤懸濁液中の着色剤表面に、懸濁液中の溶解樹脂成分を沈着させる再沈殿工程。

【特許請求の範囲】

【請求項 1】 下記工程にて、着色樹脂粒子水分散液を得る着色樹脂粒子水分散液製造方法。

(1) 酸価を有する皮膜形成性樹脂に少なくとも着色剤を分散または溶解して固形着色コンパウンドを得る樹脂着色工程。

(2) 少なくとも、水、皮膜形成性樹脂を溶解する有機溶媒、塩基、前記樹脂着色工程で得られた固形着色コンパウンドを混合し、分散によって少なくとも樹脂の一部が溶解している着色剤懸濁液を得る懸濁工程。

(3) 前記懸濁工程で得られた着色剤懸濁液中の着色剤表面に溶解樹脂成分を沈着させる再沈殿工程。

【請求項 2】 皮膜形成性樹脂を溶解する有機溶媒に、更に皮膜形成性樹脂を実質的に溶解しない親水性有機溶媒を併用する請求項 1 記載の着色樹脂粒子水分散液製造方法。

【請求項 3】 (3) の再沈殿工程において、樹脂が溶解している(2)の懸濁工程の着色剤懸濁液に、樹脂に対して貧溶媒として機能する水または水性媒体を加えるか、または樹脂を溶解する有機溶媒を懸濁液から脱溶媒する請求項 1 記載の着色樹脂粒子水分散液製造方法。

【請求項 4】 (3) の再沈殿工程において、樹脂が溶解している(2)の懸濁工程の着色剤懸濁液に樹脂に対して貧溶媒として機能する水または水性媒体を加えた後、樹脂を溶解する有機溶媒を懸濁液から脱溶媒する請求項 1 記載の着色樹脂粒子水分散液製造方法。

【請求項 5】 (1) の樹脂着色工程において、着色剤として顔料を用いて、高せん断力下で、酸価を有する樹脂にそれを分散する請求項 1 記載の着色樹脂粒子水分散液製造方法。

【請求項 6】 コンパウンドとして、着色剤としてカーボンブラックを用いて得た固形着色コンパウンドを用い、(2)の懸濁工程に次いで直ちに(3)の再沈殿工程を行うか、コンパウンドとして、着色剤として有機顔料を用いて得た固形着色コンパウンドを用いるとともに、(2)の懸濁工程と(3)の再沈殿工程との間に、高せん断力下で着色剤懸濁液中の着色剤粒子をより小粒径化する工程を設ける請求項 1 記載の着色樹脂粒子水分散液製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、着色樹脂粒子水分散液製造方法に関する。

【0002】

【従来の技術】インクジェット記録用インクは大別すると油性インクと水性インクがあるが、油性インクは臭気・毒性の点で問題があり、水性インクが主流となりつつある。

【0003】しかしながら、従来の水性インクの多くは着色剤として水溶性染料を用いているため耐水性や耐光

性が悪いという欠点を有していた。また、染料が分子レベルで溶解しているため、オフィスで一般に使用されているコピー用紙などのいわゆる普通紙に印刷すると髭状のフェザリングと呼ばれるブリードを生じて著しい印刷品質の低下を招いていた。

【0004】上記欠点を改良するためにいわゆる水性の顔料インクが過去に様々な提案されており、例えばバインダー兼分散剤として水溶性樹脂を用いてカーボンブラックや有機顔料を分散させた樹脂溶解型のインクやポリマーラテックスあるいはマイクロカプセルとして着色剤を内包する樹脂分散型のインクが各種提案されている。

【0005】ジェットプリンター用水性顔料インクとしては、なるべく微粒子径に分散された着色剤粒子が求められており、具体的な樹脂溶解型の水性インクの例として、特許第 2512861 号公報では、(a) 顔料とポリマー分散剤とを 2-ロールミリング装置に充填し；

(b) 摩砕して顔料とポリマー分散剤との分散体を得；そして(c)この顔料分散体を水性キャリア媒体中に分散させる工程からなる、改良された特性を有する水性の顔料入りインクジェット用インクの調整方法が、特開平 3-153775 号公報では、a) 顔料とカルボキシル基含有ポリアクリル系樹脂とを含有する固体顔料調合物 b) 水で希釈可能な有機溶媒 c) 湿潤剤 d) 水を含有するインクジェット印刷用水性インク組成物が提案されている。

【0006】しかしながら、これらの技術は顔料の微粒子化には有効なものの、溶解している分散剤樹脂の影響で、インクの水分蒸発に伴いノズル付近のインク粘度上昇による異常噴射や、最悪ノズル目詰まりを生じ易く、印刷物の耐水性が著しく劣っていた。

【0007】樹脂分散型の水性インクは、インクの水分蒸発に伴う粘度上昇は比較的少なく、また耐水性に優れるという利点がある。具体的には、特開昭 58-45272 号公報では染料を含有したウレタンポリマーラテックスを含むインク組成物、特開昭 62-95366 号公報では水不溶性有機溶媒中にポリマーと油性染料を溶解し、さらに表面活性剤を含む水溶液と混合して乳化させた後に溶媒を蒸発してポリマー粒子中に内包された染料を含むインクが提案され、特開昭 62-254833 号公報ではカプセル化時の有機溶媒と水との間の界面張力を 10 ダイン以下にすることによる着色料水性懸濁液の製造法が提案され、特開平 1-170672 号公報では同様にマイクロカプセル化した色素を含有する記録液等が提案されているが、それらで得られた着色樹脂分散物の分散安定性は必ずしも十分ではなく、またカプセル化時に使用する表面活性剤の影響で泡立ちが大きく、インクジェットの噴射特性が必ずしも十分ではなかった。

【0008】

【発明が解決しようとする課題】本発明が解決しようとする課題は、微粒子径で分散安定性に優れた着色樹脂粒

子水分散液製造方法を提供することにある。

【0009】

【課題を解決するための手段】本発明者等は、上記の課題を解決するために鋭意研究を重ねた結果、本発明を解決するに至った。即ち本発明は、次の発明を提供する。

【0010】下記工程にて、着色樹脂粒子水分散液を得る着色樹脂粒子水分散液製造方法。

(1) 酸価を有する皮膜形成性樹脂に、少なくとも着色剤を分散または溶解して固形着色コンパウンドを得る樹脂着色工程。

(2) 少なくとも、水、皮膜形成性樹脂を溶解する有機溶媒、塩基、前記樹脂着色工程で得られた固形着色コンパウンドを混合し、分散によって少なくとも樹脂の一部が溶解している着色剤懸濁液を得る懸濁工程。

(3) 前記懸濁工程で得られた着色剤懸濁液中の着色剤表面に溶解樹脂成分を沈着させる再沈殿工程。

【0011】本発明の(1)の樹脂着色工程は、酸価を有する皮膜形成性樹脂に、少なくとも着色剤を分散または溶解して固形着色コンパウンドを得る工程である。この工程は、例えば従来知られているロールやニーダーやビーズミル等の混練装置を用いて、溶液や加熱溶解された状態で、着色剤を、酸価を有する皮膜形成性樹脂に均一に溶解または分散させ、最終的に固体混練物(固形着色コンパウンド)として取り出すことにより行うことが出来る。

【0012】本発明において、最終的に得られる着色樹脂粒子水分散液を、ジェットインクとして用いる場合には、ジェットインクとして目詰まりがなく安定した噴射を実現する様にする。例えば、着色剤として顔料を用いる場合には、顔料の酸価を有する皮膜形成性樹脂への微分散が必要であり、顔料を分散する手段として、従来知られている分散方法のうち、相対的に高せん断力のかかる状態が形成される分散手段を採用し、高せん断力下で分散を行うことが好ましい。この様な好適な手段としては、2本ロールを用いることが好ましい。

【0013】一方、着色剤が染料の場合には、顔料と同様に混練装置を用いて染料を樹脂中に微分散させるか、染料が樹脂に溶解可能であれば、単純に染料を樹脂に溶解させればよい。

【0014】本発明の(2)の懸濁工程は、少なくとも、水、皮膜形成性樹脂を溶解する有機溶媒、塩基、前記樹脂着色工程で得られた固形着色コンパウンドを混合し、分散によって少なくとも樹脂の一部が溶解している着色剤懸濁液を得る工程である。

【0015】(1)の樹脂着色工程で得られた固形着色コンパウンドを、分散媒として水、酸価を有する皮膜形成性樹脂を溶解する有機溶媒、塩基を必須とする混合溶媒に加えて、均一に分散する様に攪拌することによって、固形着色コンパウンド表面から、着色剤を包含する酸価を有する皮膜性樹脂が、有機溶媒と塩基の助けを借

りて、溶解または自己乳化し、いずれの場合も少なくとも当該樹脂の一部が溶解している着色剤懸濁液が得られる。

【0016】この工程により、固形着色コンパウンドの表面に存在する、酸価を有する皮膜形成性樹脂は、徐々に、塩基により、その酸価の少なくとも一部又は全部が中和され、当該コンパウンドの固体形状から、混合物は懸濁状態となる。

【0017】懸濁液中の着色剤は、当該樹脂が前記液媒体に完全に溶解している場合に、は着色剤表面が露出しているが、樹脂が自己乳化している場合には、少なくとも着色剤表面の一部は樹脂で被覆されていると考えられる。着色剤が当該樹脂に溶解しうるのは、懸濁液中で、それはコロイド状態にあると考えられる。

【0018】懸濁液を得るための攪拌方法としては、公知慣用の手法がいずれも採用でき、例えば従来の1軸のプロペラ型の攪拌翼の他に、目的に応じた形状の攪拌翼や攪拌容器を用いて容易に懸濁可能である。

【0019】懸濁液を得るに当たって、せん断力がない或いは相対的に小さい、単なる混合攪拌のみで、或いは、着色剤が比較的凝集しやすい場合には、それに加えて更に、次いで高せん断力下において、より分散を安定させてもよい。この場合の分散機としては、高圧ホモジナイザーや商品名マイクロフルイダイザーやナノマイザーで知られるビーズレス分散装置等を用いるのが、着色剤の再凝集が少なく好ましい。

【0020】例えば、コンパウンドとして、着色剤としてカーボンブラックを用いて得た固形着色コンパウンドを用いる場合には、(2)の懸濁工程で、比較的小粒径に分散した着色剤懸濁液が得られるので、次いで直ちに(3)の再沈殿工程を行うことが出来る。一方、コンパウンドとして、着色剤として有機顔料を用いて得た固形着色コンパウンドを用いる場合やカーボンブラックを含めた無機顔料を用いた固形着色コンパウンドを用いる場合には、(2)の懸濁工程と(3)の再沈殿工程との間に、前者コンパウンドから得る懸濁液をより分散安定性を増すためや、後者コンパウンドから得る着色剤懸濁液中の着色剤粒子をより小粒径化するために、高せん断力下に当該懸濁液をさらして分散する工程を設けることが好ましい。

【0021】本発明の(3)の再沈殿工程は、前記懸濁工程で得られた着色剤懸濁液中の着色剤表面に、当該溶解樹脂成分を沈着させる工程である。本発明において「再沈殿」とは、着色剤、或いは当該溶解樹脂が着色剤表面に吸着した着色剤を懸濁液の液媒体から、分離沈降させることを意味するものではない。従って、この工程で得られるものは、固形成分と液体成分とが明らか分離した単なる混合物ではなく、当該溶解樹脂が着色剤表面に吸着した着色剤が懸濁液の液媒体に安定的に分散した着色樹脂粒子水分散液である。

【0022】この(2)の懸濁工程の着色剤懸濁液中の着色剤表面へ溶解樹脂の沈着は、例えば、①少なくとも一部当該樹脂が溶解している着色剤懸濁液に、当該樹脂に対して貧溶媒として機能する水または水性媒体を加えて行うか、及び／又は、②着色剤懸濁液から有機溶媒を除去して行うことによって容易に行うことが出来る。

【0023】しかしながら、着色剤懸濁液に、当該樹脂に対して貧溶媒として機能する水または水性媒体を加えて行う方法が、凝集物も少なく好ましい。再沈殿は懸濁液を緩く攪拌しながら水または水性媒体を滴下することによって、凝集物の発生を防止しながら着色剤表面に樹脂を確実に沈着(再沈殿)させることが可能となる。

【0024】この様にして(3)では、所望の粒子径の着色樹脂粒子が得られるが、通常その平均粒子径範囲は、0.01~20 μ mである。尚、分散液を最終的に、例えばインクジェット用記録液として用いる場合には、平均粒子径をサブミクロンオーダー(1 μ m未満)とすればよいし、分散液から液媒体を除去して静電気荷像現像用乾式トナーとして用いる場合には、3~15 μ mとなる様にするのが好ましい。

【0025】この様にして得られた着色樹脂粒子水分散液はそのまま用いることもできるが、共存している有機溶媒の影響で着色樹脂粒子が膨潤状態にあるため、保存安定性をより向上させるためや、或いはより火災や公害に対する安全性を高めるために、更に脱溶媒を行うことが好ましい。また、着色樹脂粒子を粉体として使用する場合には、蒸留や遠心分離・濾別等を用いて脱溶媒・脱水を行えばよい。

【0026】この様にして除去された有機溶媒は、例えば連続生産を目的とする場合には、焼却することなく、閉鎖系にてリサイクルして再利用することも出来る。

【0027】本発明の着色樹脂粒子水分散液製造方法に用いられる皮膜形成性樹脂は、酸価を有するものである。好ましい樹脂の酸価は、10~280で、(2)の懸濁工程の塩基による中和率は、(1)の当該樹脂が懸濁液中に自己乳化する程度以上あればよく、例として樹脂の酸基の10モル%以上である。高酸価樹脂の場合、塩基による中和率が高くなると懸濁液中への樹脂の溶解度が増すので、塩基の使用量は、液媒体への溶解程度や最終的に得る水分散液の分散粒子の意図する径の大小に基づき適宜調節することが好ましい。

【0028】当該皮膜形成性樹脂は、皮膜を形成する樹脂であればよく、天然樹脂や合成樹脂に限定されず様々な樹脂が用いることができ、例えばスチレン系樹脂、アクリル系樹脂、ポリエステル系樹脂、ポリウレタン系樹脂が挙げられる。当該樹脂は熱依存性のない永久架橋されたものであっても、常温では架橋しているが熱で非架橋状態となる可逆的性質の架橋を有するものであってもよい。

【0029】本発明において、皮膜形成性樹脂として好

ましい樹脂は、例えばスチレン、置換スチレン、(メタ)アクリル酸エステルからなる群から選ばれる少なくとも一つのモノマーと、(メタ)アクリル酸との共重合体である。

【0030】皮膜形成性樹脂は、懸濁過程(2)で自己乳化すると同時に、コンパウンド中で微分散している着色剤を被覆して、極めて分散安定性に優れた超微粒子着色樹脂粒子水分散液を可能とする。樹脂の分子量範囲は特に制限はないが、スチレン系樹脂やアクリル系樹脂の場合には、1000以上10万以下の分子量のものがより好ましい。

【0031】本発明の着色樹脂粒子水分散液製造方法によって得られる、サブミクロンオーダーの着色樹脂粒子水分散液は、インクジェット記録用水性インクとして用いると、分散安定性、噴射特性に優れたインクジェット適性を示す。本発明の着色樹脂粒子水分散液製造方法をこれに適用する場合、(2)の懸濁工程における懸濁液が乾燥防止剤を含有させることにより、極めて分散安定性に優れた懸濁液や水分散液さらには、水性インクが得られる。

【0032】また、(2)の懸濁工程における塩基としては、例えば水酸化ナトリウム、水酸化カリウム、水酸化リチウム等のアルカリ金属の水酸化物、アンモニア、トリエチルアミン、モルホリン等の塩基性物質の他、トリエタノールアミン、ジエタノールアミン、N-メチルジエタノールアミン等のアルコールアミンが使用可能である。

【0033】高酸価樹脂を強塩基を用いて中和を行うと、水に対する樹脂の溶解度が高まり樹脂を溶解する有機溶媒が不要になるが、(3)の再沈殿工程において着色剤表面への樹脂の沈着が不十分となるため、懸濁液中での塩基の添加量は水溶性樹脂成分が多ならないように、塩基の強さや使用量(中和率)調節することが好ましい。

【0034】特にインクジェット記録用水性インクの場合は、ノズルの目詰まりや保存時の分散安定性、印刷物の耐水性に悪影響があるため、この水溶性樹脂成分を最小限に押さえることが好ましい。アルコールアミン、特にトリエタノールアミンは弱塩基で前記水溶性樹脂成分の発生が少なく、インクジェット記録用水性インクの調製には、最適な塩基である。

【0035】本発明の着色樹脂粒子水分散液製造方法には、特に限定されるものではなく、公知慣用の着色剤がいずれも使用できるが、例えばカーボンブラック、チタンブラック、チタンホワイト、硫化亜鉛、ベンガラ等の無機顔料や、フタロシアニン顔料、モノアゾ系、ジスアゾ系等のアゾ顔料、フタロシアニン顔料、キナクリドン顔料等の有機顔料のほか、モノアゾ系、ジスアゾ系、金属錯塩系、アントラキノン系、トリアリルメタン系等の水性染料や油性染料や分散染料等の染料が用いられる。

顔料を用いるほうが、染料を用いるよりかは、耐水性に優れた着色樹脂皮膜が得られやすい。

【0036】無彩色着色樹脂粒子とりわけ黒色着色樹脂粒子を得る場合には、カーボンブラックのみ、またはそれを主体とした着色剤を用いる様にすればよいし、有彩色着色樹脂粒子を得るには、有機顔料を用いることが好ましい。上記した通り、同一の製造条件下においては、

(2)の懸濁工程で、カーボンブラックのほうが、有機顔料より小粒径とすることが容易である。

【0037】かかる着色剤の使用量は、本発明における効果を達成すれば特に規定されないが、最終的に得られる着色樹脂粒子分散液中で、通常0.5～20重量%となるような量となる様に調製するが好ましい。ジェット記録用水性インクを得る場合も同様である。

【0038】(2)の懸濁工程に用いられる分散媒は、主体は貧溶媒として機能する水であり、最終的に得られる着色樹脂粒子水分散液をインクジェット記録用水性インクとして用いる場合には、本発明の各工程或い付加的に行われる工程の全てにおいて、液媒体は、イオン交換水以上の純度を有することが好ましい。

【0039】本発明では、酸価を有する皮膜形成性樹脂を溶解する有機溶媒が用いられるが、これは当該樹脂に対して良溶媒として機能するものである。当該有機溶媒としては、当該樹脂に対して適宜選択することが出来、例えばアセトン、ジメチルケトン、メチルエチルケトン等のケトン系溶媒、メタノール、エタノール、イソプロピルアルコール等のアルコール系溶媒、クロロホルム、塩化メチレン等の塩素系溶媒、ベンゼン、トルエン等の芳香族系溶媒、酢酸エチルエステル等のエステル系溶媒、エチレングリコールモノメチルエーテル、エチレングリコールジメチルエーテル等のグリコールエーテル系溶媒、アミド類等樹脂を溶解させるものであれば使用可能である。

【0040】(2)の懸濁工程では、水及び有機溶媒の混合液が均一であることが好ましく、均一でない場合は、界面活性剤を用いるか、あるいは機械的にO/W型に乳化させるか、助溶媒を併用して均一化させて用いることが好ましい。

【0041】即ち、分散媒を形成する、酸価を有する皮膜形成性樹脂を溶解する有機溶媒は、そのみを用いる様にしてもよいが、それと水と塩基のみで、分散安定性に優れた着色剤懸濁液を得難い場合には、それに、酸価を有する皮膜形成性樹脂を溶解しない親水性有機溶媒を、助溶媒として一部併用してより良い安定性を持たせる様にしてもよい。尚、酸価を有する皮膜形成性樹脂を溶解する有機溶媒及び同溶解しない有機溶媒は、いずれも1種又は2種以上を併用してもよい。

【0042】当該皮膜形成性樹脂が、例えばスチレン、置換スチレン、(メタ)アクリル酸エステルからなる群から選ばれる少なくとも一つのモノマーと、(メタ)ア

クリル酸との共重合体の場合には、メチルエチルケトン等のケトン系溶媒を主として、助溶媒としてイソプロピルアルコール等のアルコール系溶媒から選ばれる少なくとも1種類以上の組み合わせが良い。

【0043】かかる水と有機溶媒の比率は、本発明における効果を達成すれば特に規定されないが、水/有機溶媒の重量比が10/1～1/1となるような量が好ましい。皮膜形成性樹脂を溶解しない親水性有機溶媒を併用する場合には、その使用量は最小限にとどめることが、最終的に得る分散液を、出来るだけ有機溶媒を含まない液媒体を分散媒としたものとする点や、混合溶剤の分離回収処理の負担をより軽減する点からも好ましい。

【0044】上記有機溶媒には、添加剤として、必要に応じて分散剤、可塑剤、酸化防止剤、紫外線吸収剤等を用いても良いし、また同様に(1)の着色工程に加えても良い。

【0045】また上記で得られた分散液を、インクジェット記録用インクとして用いる場合には、インクの乾燥を防止するために、乾燥防止剤を当該インク中に存在させておくのが好ましい。当該乾燥防止剤は、(2)の懸濁工程あるいは最終的に得られた着色樹脂粒子水分散液に直接添加すれば良い。

【0046】かかる乾燥防止剤は、インクジェットの噴射ノズル口でのインクの乾燥を防止する効果を与えるものであり、通常水の沸点以上の沸点を有するものが使用される。このような乾燥防止剤としては、従来知られている公知慣用のものがいずれも使用できるが、例えばエチレングリコール、プロピレングリコール、ジエチレングリコール、ジプロピレングリコール、ポリエチレングリコール、ポリプロピレングリコール、グリセリン等の多価アルコール類またはそれらのアルキルエーテル類、等がある。

【0047】乾燥防止剤の使用量は、種類によって異なるが、通常、水100重量部に対して1～150重量部の範囲から適宜選択される。

【0048】特に本発明の製造方法を、インクジェット記録用水性インクの製造方法に適用する場合においては、グリセリンが乾燥防止剤の場合に最も優れた乾燥防止効果を示す。グリセリンの使用量は、通常、水100重量部に対して、グリセリンのみ及びそれに他の乾燥防止剤を併用したものをを使用する場合には、10～50重量部が好適である。

【0049】特に本発明の製造方法を、インクジェット記録用水性インクの製造方法に適用する場合においては、必要に応じて、インクを紙によりよく浸透させるための浸透性付与剤として、浸透性付与効果を示す水溶性有機溶媒、水溶性樹脂、pH調整剤、分散・消泡・紙への浸透のための界面活性剤、防腐剤、キレート剤等の添加剤を加えることができる。

【0050】これら添加剤は、予め水性媒体中に添加し

ても、着色剤を含む自己水分散性樹脂溶液と水性媒体とを混合するときに添加しても、また、それらの混合後に添加してもよい。

【0051】特に本発明の製造方法を、インクジェット記録用水性インクの製造方法に適用する場合においては、得られた分散液はそのまま水性インクとして用いることが出来るが、通常は、所望の粒径のフィルターに通過させ濾過して、インクジェット記録装置のノズル径よりも小さい粒子のみが液媒体に分散したインクジェット記録用水性インクとして使用に供される。従って、この用途の場合には、好ましくは最終濾過後に添加剤を添加するのは、避けたほうがよい。

【0052】本発明の着色樹脂粒子水分散液製造方法によって得られる着色樹脂粒子は、分散液の状態、或いは乾燥した粉体の状態で、透明性、発色性、分散安定性に優れていることから、インクジェット記録用水性インクの他、他のインク一般、塗料、カラーフィルターへの応用が可能で、また樹脂の酸価と塩基による中和率の組合せによって粒子径も任意に制御可能であるため、静電荷現象用トナー等の分野にも応用が可能である。

【0053】

【発明の実施の形態】本発明は次の実施形態を含む。

【0054】1. 下記工程にて、着色樹脂粒子水分散液を得る着色樹脂粒子水分散液製造方法。

(1) 酸価を有する皮膜形成性樹脂に少なくとも着色剤を分散または溶解して固形着色コンパウンドを得る樹脂着色工程。

(2) 少なくとも、水、皮膜形成性樹脂を溶解する有機溶媒、塩基、前記樹脂着色工程で得られた固形着色コンパウンドを混合し、分散によって少なくとも樹脂の一部が溶解している着色剤懸濁液を得る懸濁工程。

(3) 前記懸濁工程で得られた着色剤懸濁液中の着色剤表面に溶解樹脂成分を沈着させる再沈殿工程。

【0055】2. 皮膜形成性樹脂を溶解する有機溶媒に、更に皮膜形成性樹脂を実質的に溶解しない親水性有機溶媒を併用する、上記1記載の着色樹脂粒子水分散液製造方法。

【0056】3. (3)の再沈殿工程において、樹脂が溶解している(2)の懸濁工程の着色剤懸濁液に、樹脂に対して貧溶媒として機能する水または水性媒体を加えるか、または樹脂を溶解する有機溶媒を懸濁液から脱溶媒する、上記1又は2記載の着色樹脂粒子水分散液製造方法。

【0057】4. (3)の再沈殿工程において、樹脂が溶解している(2)の懸濁工程の着色剤懸濁液に樹脂に対して貧溶媒として機能する水または水性媒体を加えた後、樹脂を溶解する有機溶媒を懸濁液から脱溶媒する、上記1又は2記載の着色樹脂粒子水分散液製造方法。

【0058】5. (1)の樹脂着色工程において、着色剤として顔料を用いて、高せん断力下で、酸価を有する

樹脂にそれを分散する、上記1～4記載の着色樹脂粒子水分散液製造方法。

【0059】6. (1)の樹脂着色工程において、着色剤として顔料を用いて、二本ロールを用いて、酸価を有する樹脂にそれを分散する、上記1～4記載の着色樹脂粒子水分散液製造方法。

【0060】7. コンパウンドとして、着色剤としてカーボンブラックを用いて得た固形着色コンパウンドを用い、(2)の懸濁工程に次いで直ちに(3)の再沈殿工程を行うか、コンパウンドとして、着色剤として有機顔料を用いて得た固形着色コンパウンドを用いるとともに、(2)の懸濁工程と(3)の再沈殿工程との間に、高せん断力下で着色剤懸濁液中の着色剤粒子をより小粒径化する工程を設ける、上記1～6記載の着色樹脂粒子水分散液製造方法。

【0061】8. 酸価を有する皮膜形成性樹脂が、酸価10～280の酸基を有する皮膜形成性樹脂であり、塩基が、酸基を有する皮膜形成性樹脂の酸基の10モル%以上である上記1～7記載の着色樹脂粒子水分散液製造方法。

【0062】9. 酸価を有する皮膜形成性樹脂が、スチレン、置換スチレン、(メタ)アクリル酸エステルからなる群から選ばれる少なくとも一つのモノマーと、(メタ)アクリル酸との共重合体である上記1～7記載の着色樹脂粒子水分散液製造方法。

【0063】本発明の好適な実施の形態を、インクジェット記録用インクに適用した場合を例にして説明すると、以下の通りである。

【0064】(1)カルボキシル基に基づく酸価を有する皮膜形成性スチレンー(メタ)アクリル酸共重合体樹脂に、着色剤としての顔料を二本ロールを用いて分散して、固形着色コンパウンドを得る。

【0065】(2)水、前記樹脂を溶解する良有機溶媒を主として、前記樹脂を実質的に溶解しない貧有機溶媒を、前者良溶媒の割合が大きくなる様に併用して、塩基としてのアルコールアミン、乾燥防止剤を各々含む、水を主液媒体とする溶液を調製しそれに、前記工程(1)の固形着色コンパウンドのチップを混合し、攪拌によって着色剤懸濁液を得る。より好適には懸濁液を、高せん断力を与えることが出来、より充分な懸濁状態が得られる分散機であるナノマイザー(商標)を用いて、再凝集が無い様に、さらに微粒子化を行う。

【0066】(3)着色剤懸濁液を攪拌しながら、乾燥防止剤を含む水溶液を滴下し、着色樹脂粒子水分散液を得る。

【0067】得られた着色樹脂粒子水分散液から、有機溶媒を留去し、インクベースとする。このインクベースに、インク調整用薬剤を加え、濃度・物性を調整した後、ろ過を行いインクジェット記録用水性インクとする。

【0068】

【実施例】次に実施例及び比較例を挙げて本発明を更に具体的に説明する。尚、以下の実施例中における「部」は『重量部』を表わす。

【0069】（実施例1）カーボンブラック20部とスチレン-アクリル酸-メタクリル酸樹脂（スチレン/アクリル酸/メタクリル酸=77/10/13；分子量5万・酸価160）20部の二本ロール混練物を、水210部、グリセリン35部、トリエタノールアミン8部、メチルエチルケトン90部、イソプロピルアルコール40部の混合溶液に入れ、室温で3時間攪拌し着色剤懸濁液を得た。

【0070】得られた懸濁液に攪拌しながら、グリセリン30部と水210部の混合液を毎分5mlの速度で滴下し、黒色着色樹脂粒子水分散液を得た。得られたカプセル液をロータリーエバポレーターを用いてメチルエチルケトンとイソプロピルアルコールを留去し、最終の黒色着色樹脂粒子水分散液を得た。

【0071】この水分散物を1 μ mフィルターを用いてろ過を行い、インクジェット記録用水性インクとした。

【0072】得られた水性インク中のマイクロカプセルは0.09 μ mの平均粒子径を有しており、凝集物もなく長期にわたって安定な分散を示し、ピエゾ式インクジェットプリンターを用いた印字は安定しており、得られた印刷物は滲みもなく高い黒色度を示し、しかも耐水耐光性に優れていた。

【0073】（比較例1）メチルエチルケトン（皮膜形成性樹脂を溶解する良有機溶媒）を除いた以外は実施例1の懸濁液組成で、二本ロール混練物の攪拌を実施例1と同様に行ったが、混練物は溶解せず懸濁液が得られずインク化することができなかった。

【0074】（実施例2）キナクリドン顔料40部とス

チレン-アクリル酸-メタクリル酸樹脂（スチレン/アクリル酸/メタクリル酸=77/10/13；分子量5万・酸価160）40部の二本ロール混練物を、水250部、グリセリン22部、トリエタノールアミン8部、メチルエチルケトン90部、イソプロピルアルコール40部の混合溶液に入れ、室温で3時間攪拌し混練物が溶解したところで、衝突式分散機ナノマイザー（ナノマイザー社製）を用いて98MPaの圧力で分散を行い着色剤懸濁液を得た。

【0075】得られた懸濁液に攪拌しながら、グリセリン22部と水250部の混合液を毎分5mlの速度で滴下し、マゼンタ色着色樹脂粒子分散液を得た。得られたカプセル液をロータリーエバポレーターを用いてメチルエチルケトンとイソプロピルアルコールを留去し、最終のマゼンタ色着色樹脂粒子水分散液を得た。

【0076】この水分散物を1 μ mフィルターを用いてろ過を行い、インクジェット記録用水性インクとした。

【0077】得られた水性インク中の着色樹脂粒子は0.12 μ mの平均粒子径を有しており、凝集物もなく長期にわたって安定な分散を示し、ピエゾ式インクジェットプリンターを用いた印字は安定しており、得られた印刷物は滲みもなく、透明感の高い極めて鮮やかなマゼンタ色を示し、しかも耐水耐光性に優れていた。

【0078】

【発明の効果】本発明の着色樹脂粒子水分散液製造方法により得られる着色樹脂粒子水分散液中の着色樹脂粒子は微粒子径で、極めて分散安定性に優れており、例えばインクジェット記録用水性インクに適用すると、印刷品質・耐水性・耐光性に優れた樹脂分散型水性インクの特長を殺すことなく、分散安定性に優れ、かつノズル目詰まりもなく、安定したインクジェット噴射特性を可能にする。